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AFRL

THE AIR FORCE RESEARCH LABORATORY
LEAD | DISCOVER | DEVELOP | DELIVER



Synthesis of Backfunctionalized Imidazolinium Salts and NHC Carbene Complexes

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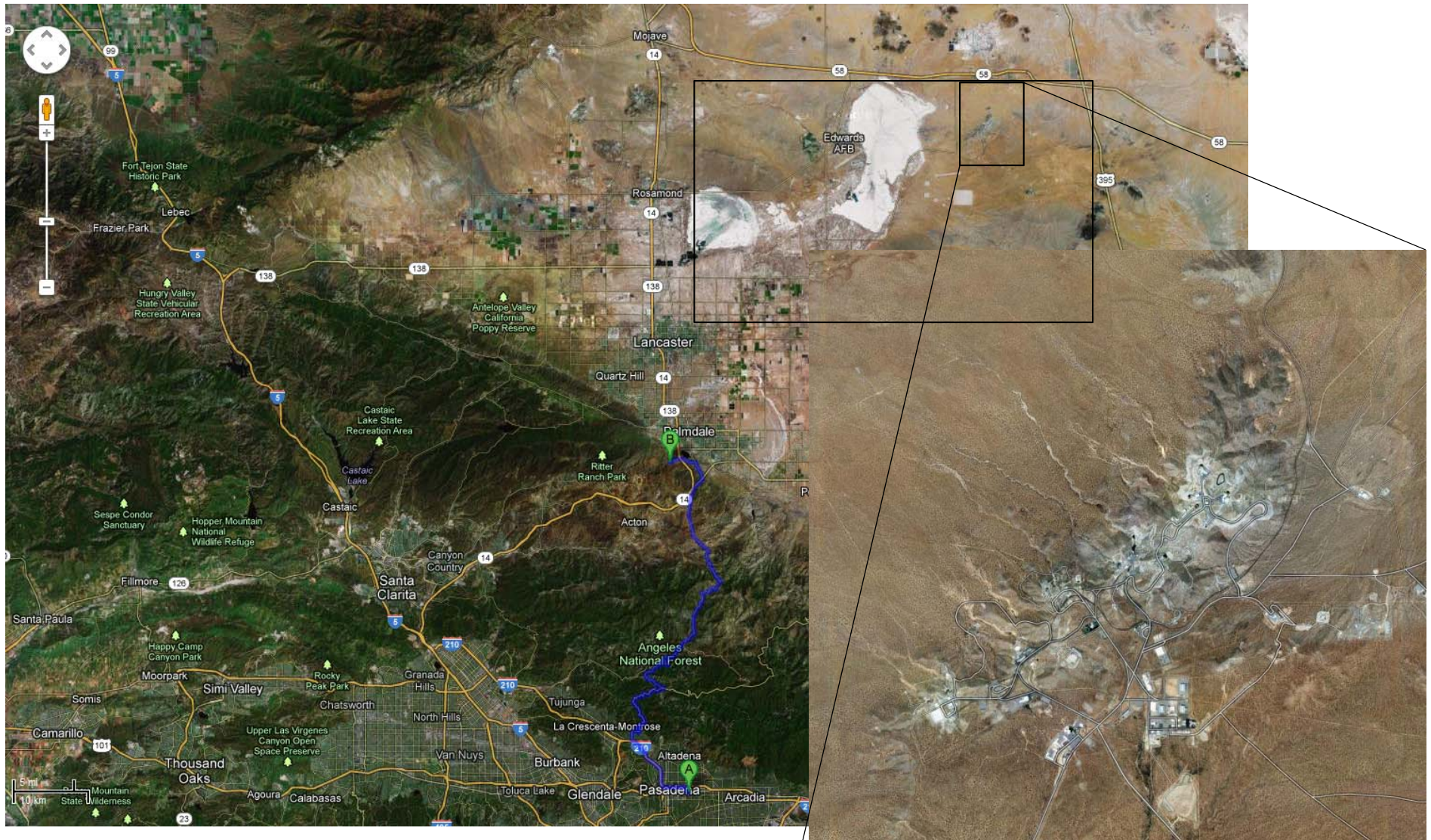
Introduction



- **Introduction**
- **Research Overview**
- **Synthesis of Backfunctionalized Imidazolinium salts and NHC carbene complexes**
 - Initial Research
 - Unintended Discovery
 - Survey chemistry of aromatic systems
 - Expansion of survey chemistry to aliphatics
- **Conclusions and Future Directions**



Edwards AFB – AFRL Rocket Propulsion Research



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Edwards AFB



- **History**

- Originally known as Muroc Army Air Corps Base
- Test flights of the YB-42 (first American Jet) in the early '40s
- Location where Chuck Yeager broke the Sound Barrier in the Bell X-1 (Original craft at the Smithsonian)
- X-15 sub-orbital flights in the '60s (Armstrong)

- **AFRL**

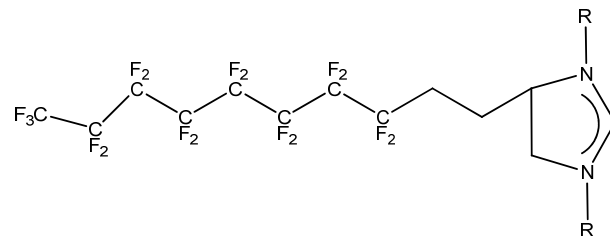
- Tenant of Edwards AFB since late '50s
- Full scale testing of the Atlas rockets (Gemini missions)
- Initial testing of the F-1 engine (Apollo missions) performed on site in the mid '60s
- Large scale testing of solid rocket motors (Titan IV)
- “Iranian nuclear facility” destroyed by the Transformers in “Transformers: The Dark side of the Moon”



Edwards AFB – AFRL Projects



- **The Air Force has an interest in NHC carbene precursors for a variety applications**
 - Ionic liquid propellants and additives
 - Ligands for Supercritical Chemical Fluid Deposition (SCFD)
- **The Air Force also has an interest in fluorinated NHC carbenes**
 - perfluoroalkyl chains generally known to improve solubility of systems in supercritical fluids
 - “Backfluorinated” NHC carbenes to improve solubility in supercritical fluids and maintain ligand stability

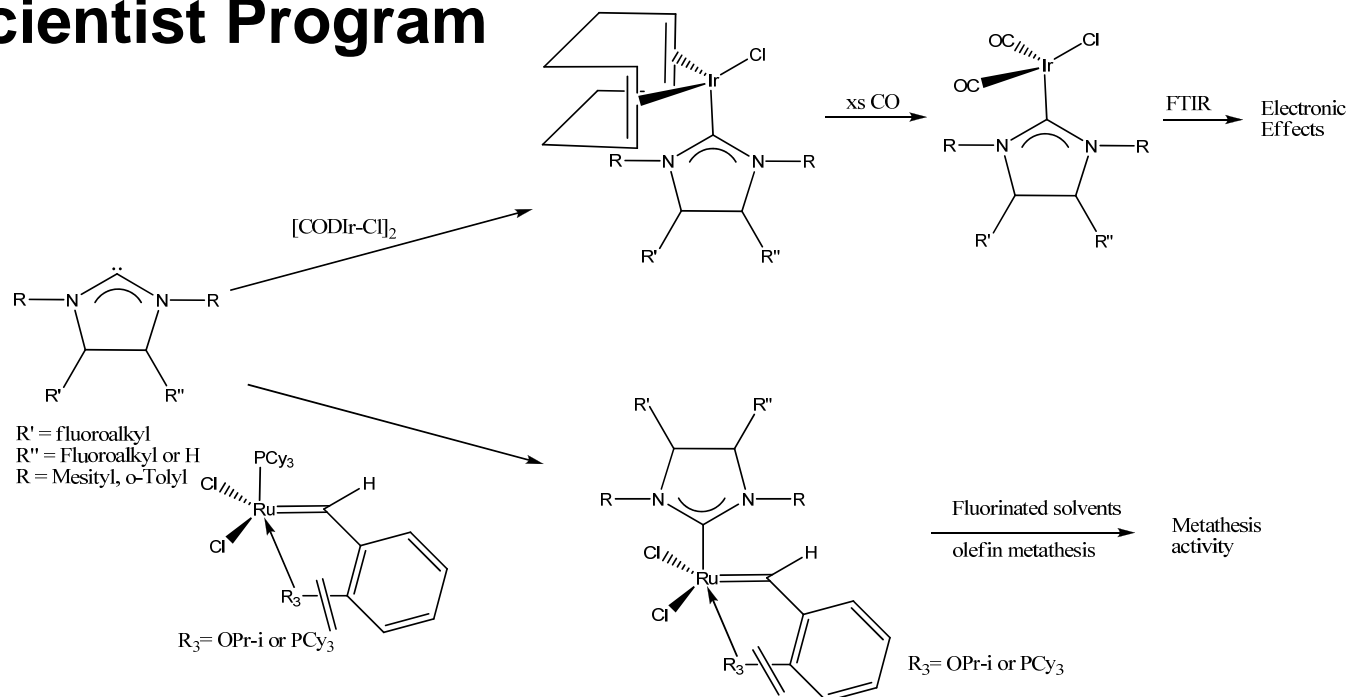




Backfluorinated NHC-Ru Catalysts Overlaying Two Technologies



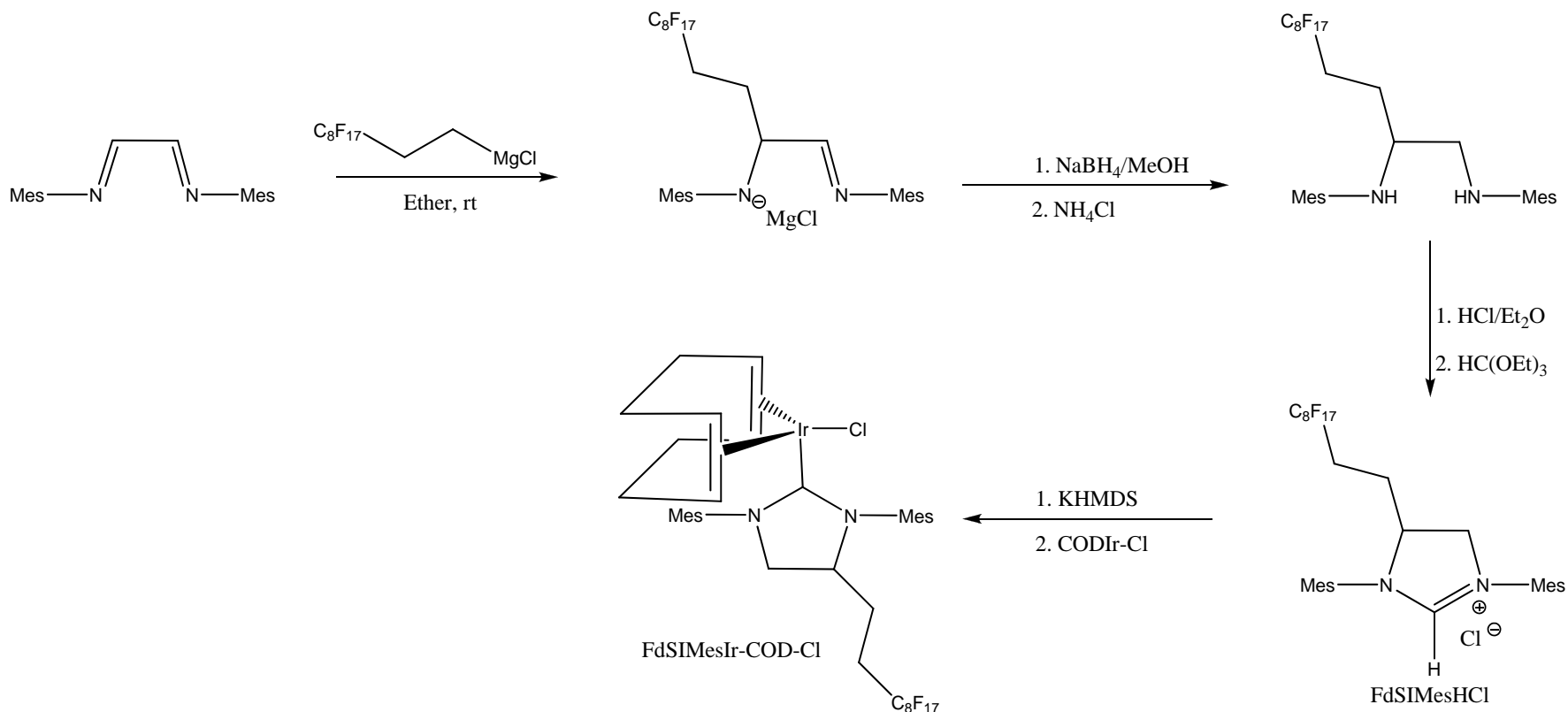
- It was easy to see that this technology should be applicable to other research areas
 - Olefin metathesis
- A Sabbatical was completed with Grubbs through the Visiting Scientist Program



<http://www.dtic.mil/dtic/tr/fulltext/u2/a623502.pdf>



Synthesis of Backfluorinated NHC Carbenes



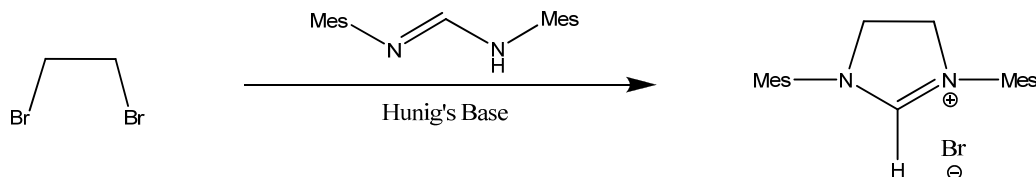
- Methodology is effective but inefficient
- Is there a more efficient method to synthesize?



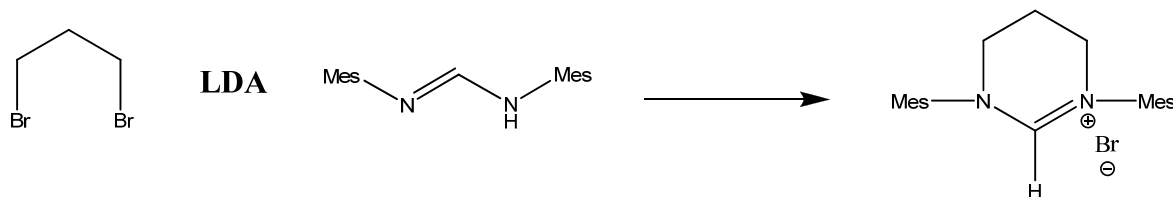
Backfluorinated NHC Carbenes Is There a Better Synthetic Method?



- **Maybe!**
- **What about a cyclization with a formamidine and a fluorinated dihalide?**
 - Inspired by Grubbs' and Bertrand's work



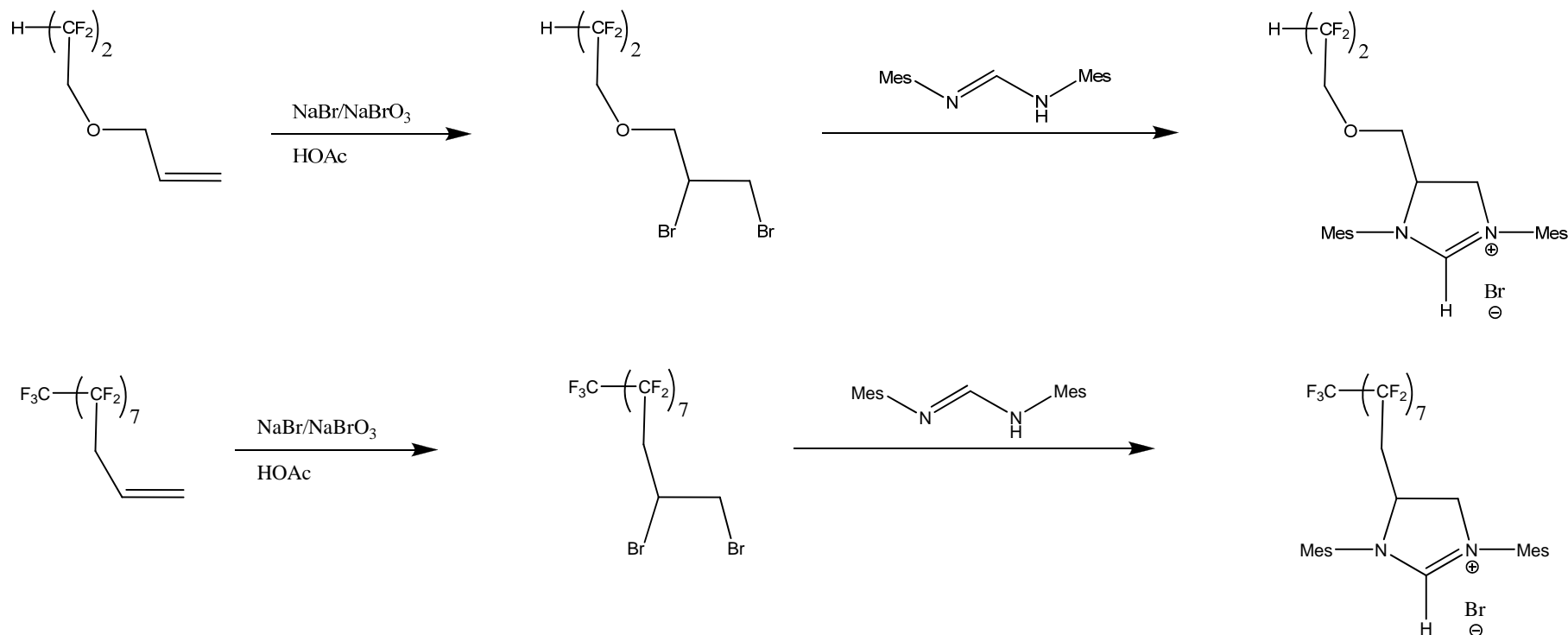
Kuhn and Grubbs - Org. Lett., 2008, 10, 2075



Bertrand - JOMC,691 (2006), 3201–3205



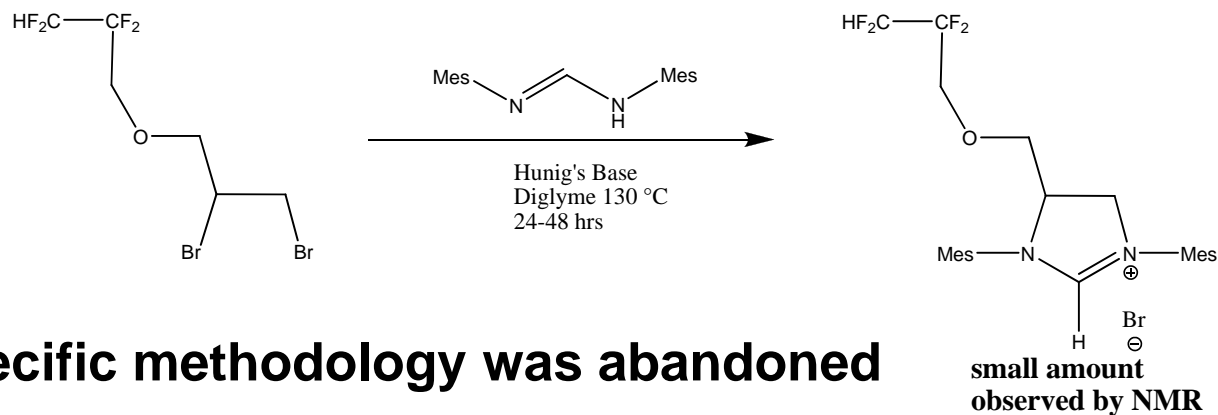
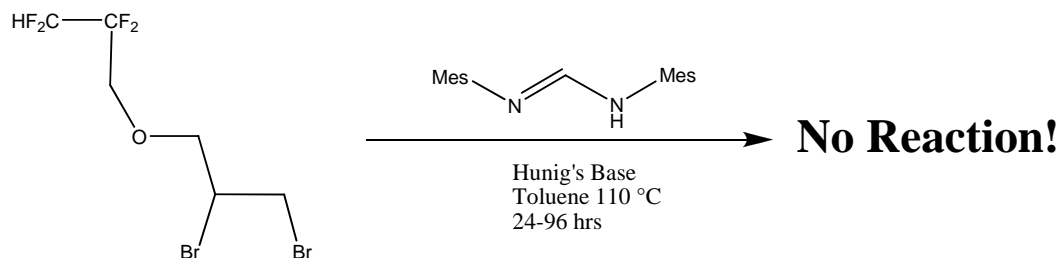
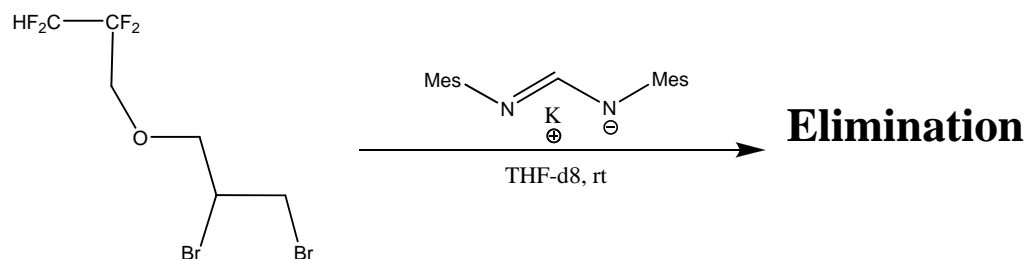
Backfluorinated NHC Carbenes Cyclization with Formamidinium



- **Tetrafluoropropyl group chosen as simulant**
 - Determine optimal reaction conditions with very cheap reagent (10 cents/gram)



Cyclization with Formamidine Secondary Substitution an Issue

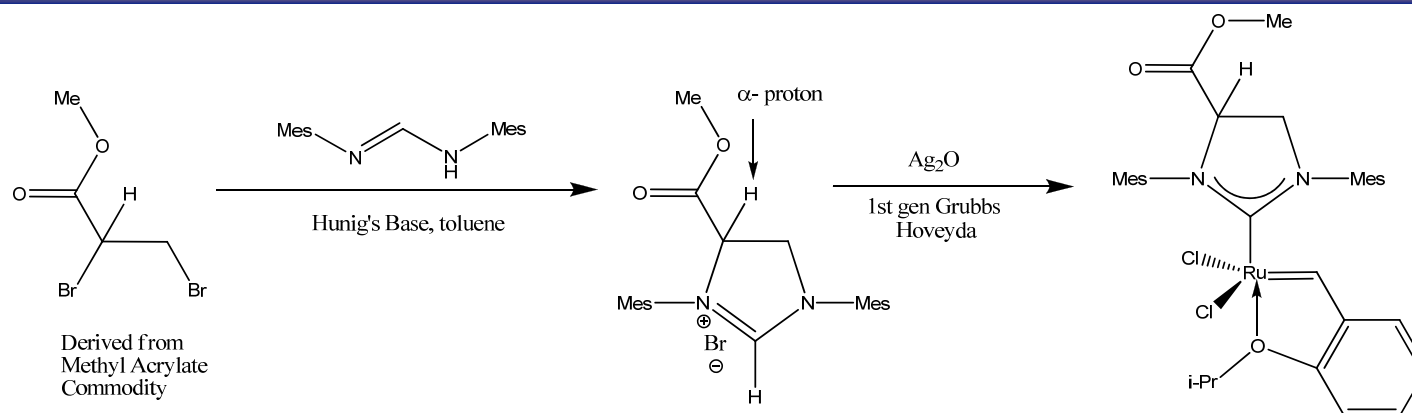


- This specific methodology was abandoned



Grubbs Lab Discovery

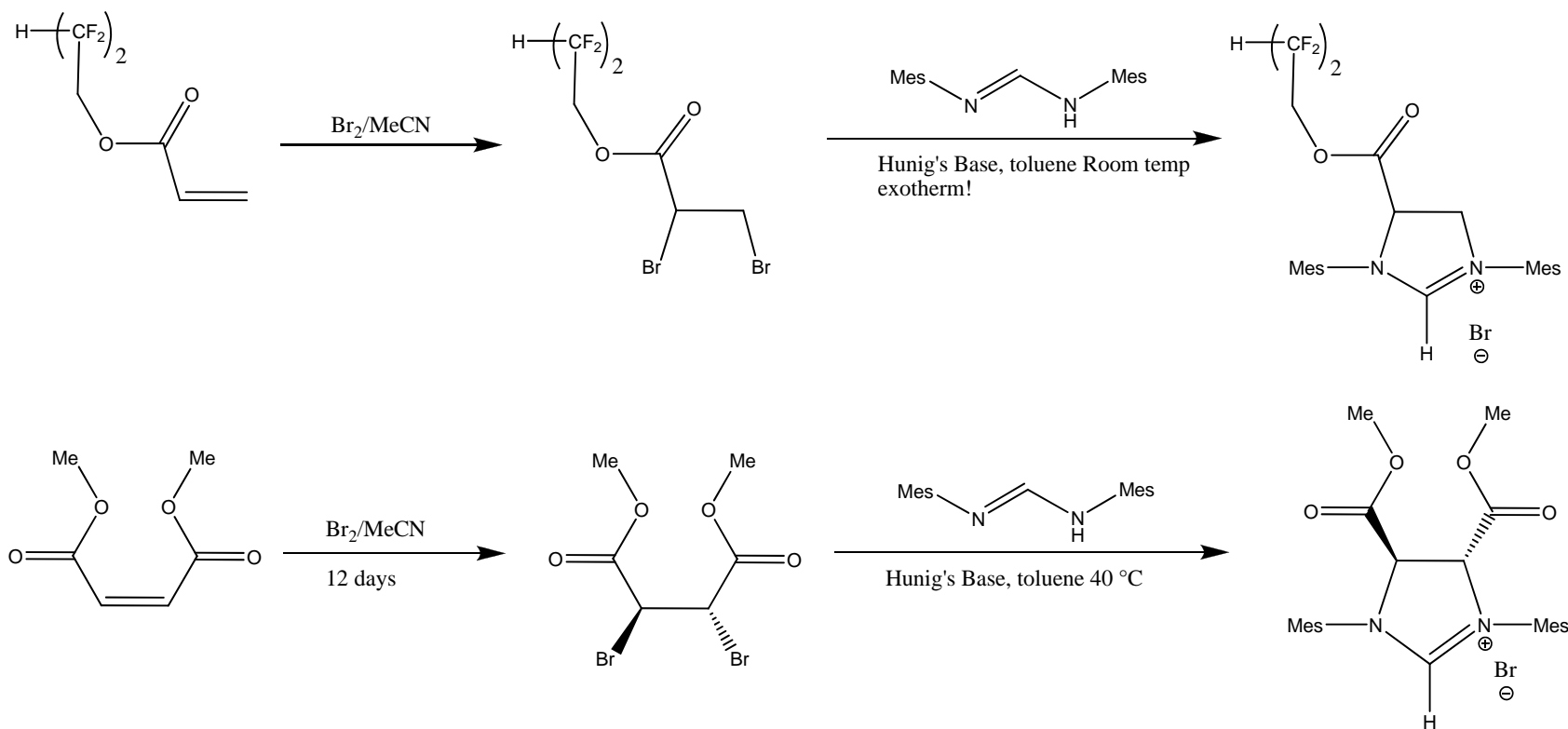
Myles Herbert – PhD Grubbs 2014



- During my stay at Caltech, Myles presented that methyl-2,3-dibromopropionate can be cyclized with mesityl formamidine to give the imidazolinium salt in high yield
- The activity of the synthesized metathesis catalyst is comparable to the unsubstituted catalyst
 - Backfunctionalization minimally perturbs ligand electronics
- Project was dropped for Z-selective work
- Can this methodology be used for backfluorinated NHC carbene complexes?



Backfunctionalized Imidazolinium Salts Mono and Difunctional



- Original cyclization work required elevated temperatures for completion
- Exotherm suggests ester group may affect electronics

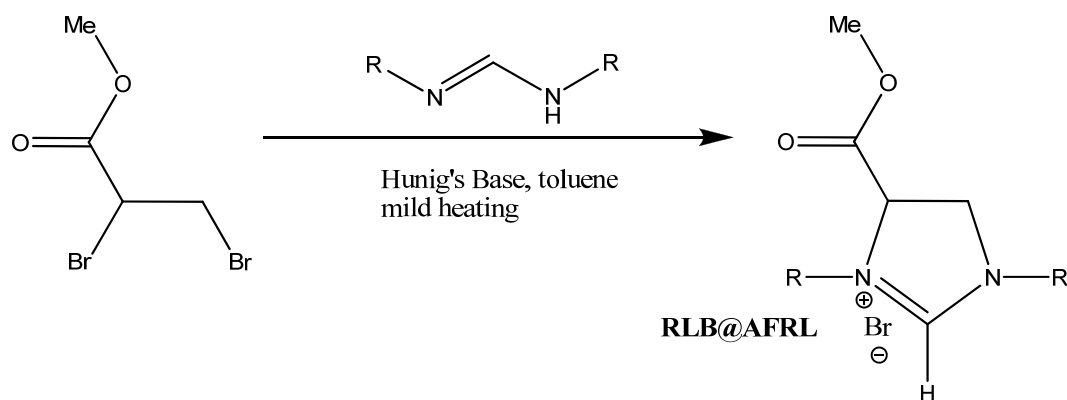


Backfunctionalized Imidazolinium Salts

Fleshing out the limits of cyclization



- Aromatic and bulky aliphatic groups are cyclized
- Aromatics with e^- withdrawing groups (Ar_f , $C_6F_5^-$, $o\text{-CF}_3\text{-Ar}$, $m\text{-CF}_3\text{-Ar}$, $1,3,5\text{-F}_3C_6H_2^-$) not cyclized
- Can other aliphatics be cyclized?

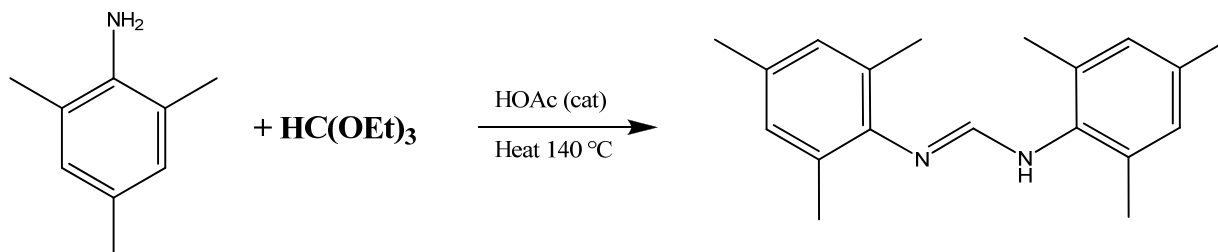


FROMAMIDENE PRECURSOR	PRODUCT	ADDITIONAL NOTE
mesityl	Colorless solid	75%, unoptimized
o-tolyl-	Colorless solid	
p-tolyl-	Colorless solid	
2,6-diisopropylphenyl-	Colorless solid	
4-CF ₃ -phenyl-	Colorless solid	50%
adamantyl-	Colorless solid	
cyclohexyl-	Colorless solid	
2-ethyl-1-hexyl-	Yellow viscous oil	Toluene soluble!

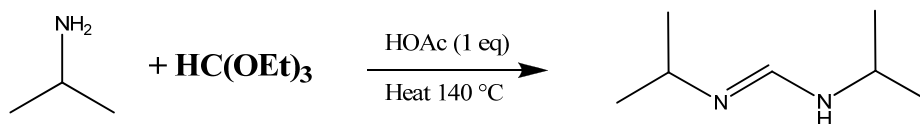
US Patent App 20160102061



Synthesis of Formamidines Low Boiling Amines Issue



- Using HOAc as a catalyst worked for all high boiling amines/anilines but not suitable for low boiling amines
- Issue of lower boiling amines solved by Cavell
- One equivalent of HOAc to form nonvolatile salt
 - Adapted procedure to other aliphatic amines



Cavell - Dalton Trans., 2013, 42, 7318–7329

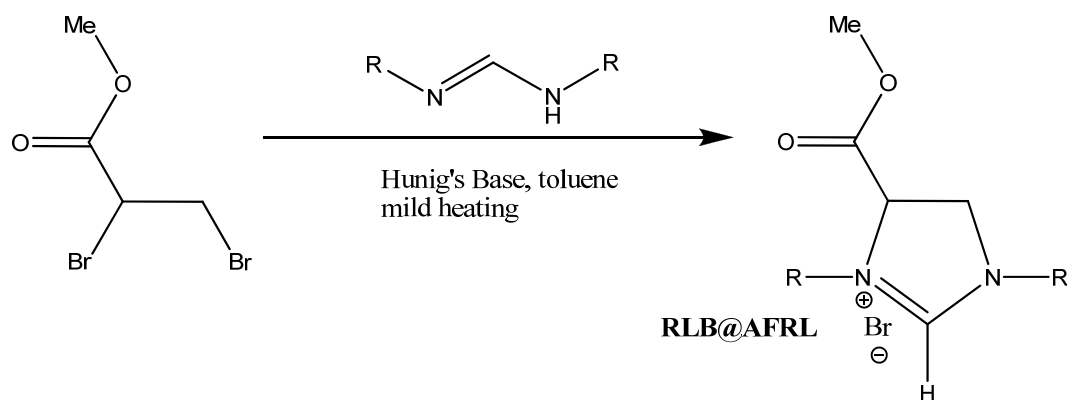


Backfunctionalized Imidazolinium Salts

Fleshing out the limits of cyclization



- All aliphatic groups attempted are cyclized
- All fall under the definition of “ionic liquid”
- All are toluene soluble
- Constitutes a new class of materials: backfunctionalized ionic liquids

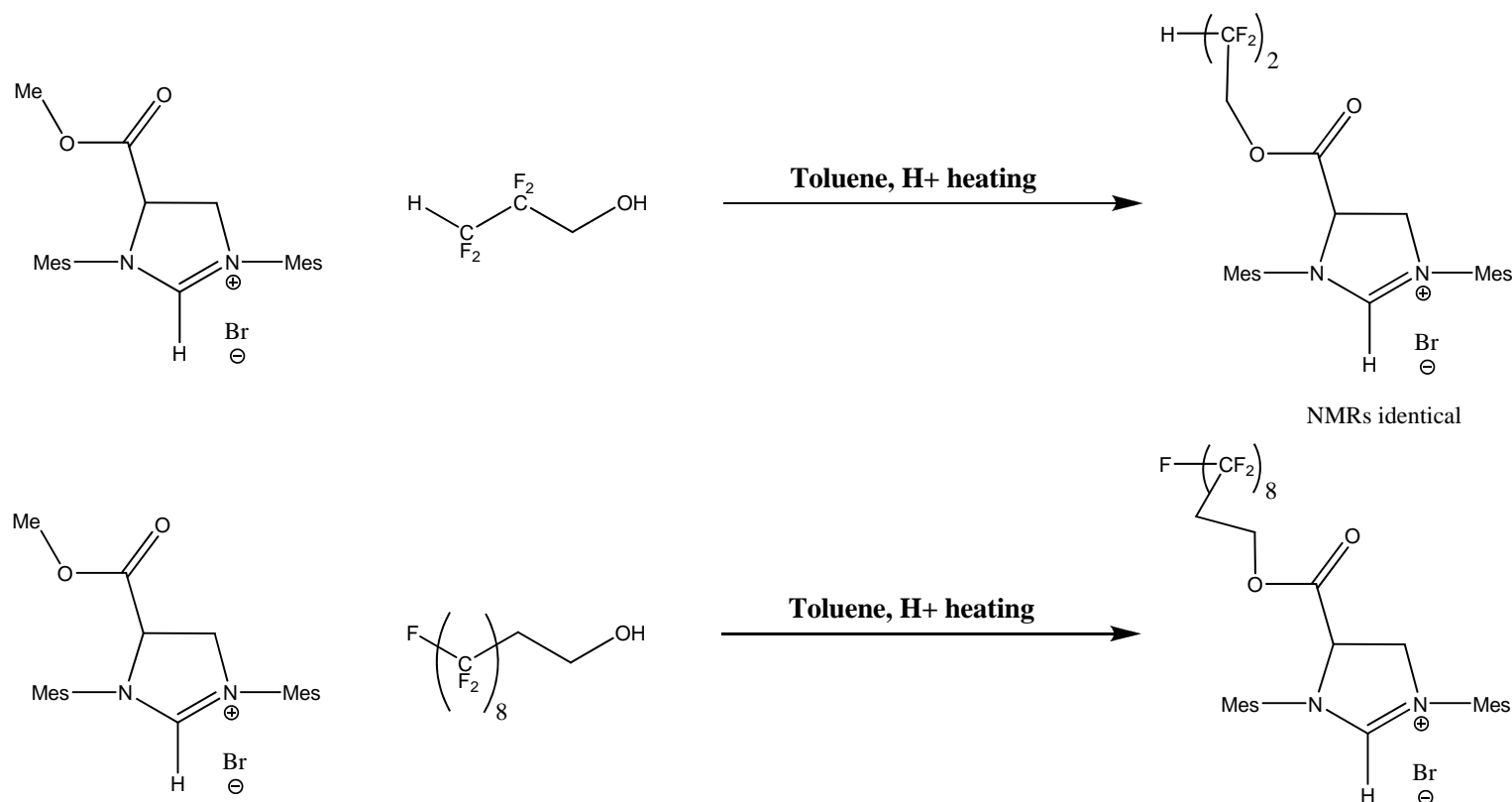


FROMAMIDENE PRECURSOR	PRODUCT	ADDITIONAL NOTE
Methyl-	TBD	
n-propyl-	Yellow viscous oil	
i-propyl-	Yellow viscous oil	
n-butyl-	Yellow viscous oil	
sec-butyl	Yellow viscous oil	
iso-butyl	Yellow viscous oil	
tert-butyl	Yellow viscous oil	
n-hexyl	Yellow viscous oil	Toluene soluble

US Patent App 20160102061



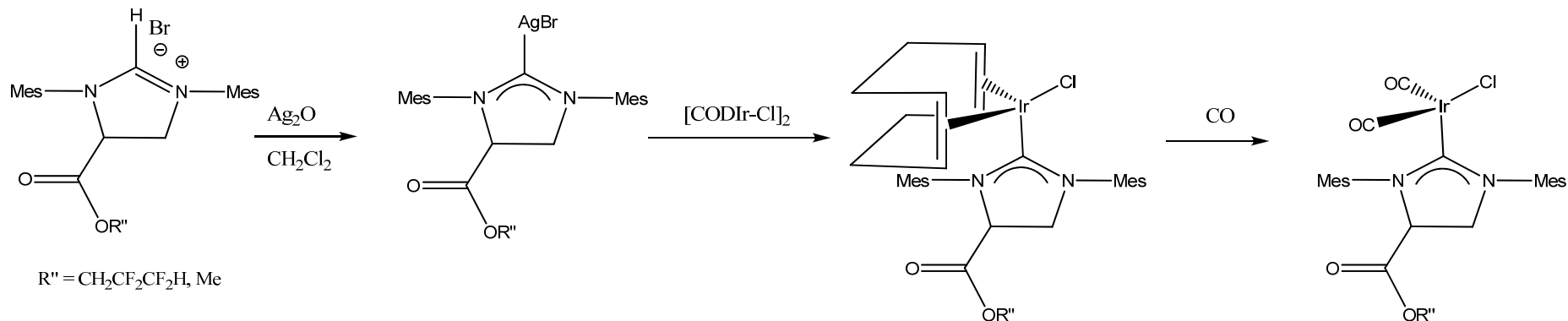
Backfunctionalized Imidazolinium Salts Transesterification



- Transesterification is effective
- Exploring other possibilities → Exotic groups
- Adds to the enormous potential of the technology



Backfunctionalized NHC Complexes Iridium Compounds



- Standard Ag metalation conditions
- Electronics study pending



Backfunctionalized Imidazolinium Salts



- **Conclusions**
 - **Backfunctionalization by the cyclization of a formamidine with a secondary dihalide is not effective**
 - **One exception is the cyclization of a brominated acrylate with mesityl formamidine**
 - **The cyclization of a brominated acrylate and a formamidine is quite general**
 - **In addition to the aromatic imidazolinium salts prepared, a new class of backfunctionalized imidazolinium-based ionic liquids was also invented**



Future Work



- **Perform detailed electronics study on ligands**
- **Increase the amount of backfluorination of imidazolinium complexes (difunctional)**
- **Look for strategic collaborations to push the technology forward**
- **Investigate the use of the technology for other applications in order to improve sustainability**
 - **Dual Use Technology**



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- **Grubbs Group**